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# BIOMIMETICS

## Design and Processing
of Materials

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# BIOMIMETIC CERAMICS AND HARD COMPOSITES

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*Biological structural materials are all composites and have sophisticated microstructures which allow good properties to be realized by rather weak polymers and minerals. By coupling these microstructures with strong synthetic polymers and ceramics, we could hope to produce high performance materials. This article reviews the properties of hard biological materials to provide a basis for comparison with synthetics, and discusses how biomimetic composites and ceramics may be produced.*

## 1.0 INTRODUCTION

Structural biological materials are all composites. The basic structural units include elastomers, strong polymers, and reinforcing minerals. These components are mixed in various proportions and with various architectures to produce a wide range of mechanical properties. Combinations of hardness with toughness and of softness with strength can give rise to mechanical responses which seem to be superior to the equivalent synthetic materials.

The superior sophistication is easily seen by a comparison between micrographs of the complex morphology of bone or shell and of the equivalent ceramics or filled polymers. It is less easy to prove a superiority of properties since the component materials of bone, collagen, and hydroxyapatite cannot be regarded as high performance materials when compared to carbon fiber and polyimide. We therefore must make comparisons on a basis which allows for the different starting properties of the component materials. Assuming that we can convince ourselves of a performance improvement which arises from the material architecture we should consider how to develop synthetic materials with equivalent microstructures.

A second case may be considered, that biological materials do not prove to be superior in strength, toughness or any simple combination of properties but are desirable structures because they integrate better with the overall mechanical design of the system. In this case we are suggesting that the ability to locally tune mechanical properties allows a stronger structure to be built than if the machine was constructed from simple materials joined at sharp interfaces. Biomimicry in this case would require a conjunction of materials science, processing, and design engineering that is unlikely to occur in the short term.

Our approach has been to accept that the superiority of biological structures will be demonstrated and to consider what methods can be used to reproduce them synthetically. We have concentrated on hard composites and ceramics produced by the precipitation of inorganic reinforcing particles into a polymer matrix. There clearly are other approaches, ranging from perversion of a truly biological system to produce more useful materials to the use of existing processing methods to form more complex structures. In this paper I will review the features which we would like to see in a true mimicry of biomineralization and the progress which we have made towards this.

## 2.0 STRUCTURES OF BIOLOGICAL AND SYNTHETIC MATERIALS

The structural biological polymers include the polysaccharides, cellulose and chitin and the proteins, silk, elastin, and collagen. Cellulose and silk are highly oriented fibers with properties that are comparable with highly drawn Nylon or polyester fibers. The biological fibers are made through aqueous chemistry and are consequently much more hydrophilic, and much more plasticized by water, than are the synthetics. This water sensitivity has of course been the source of most of the drawbacks that wood has as a construction material, particularly its tendency to dry and split. An equivalent problem for the synthetic fibers is that melt spun fibers are limited to a melting point at which degradation can be avoided and so inter-chain bonding is kept relatively weak, compared to the high levels of hydrogen bonding in cellulose or silks. Silk is used primarily as a fiber, but cellulose and collagen occur in bulk though always basically in fiber form. It is interesting that biology has not used the strong polymers in unoriented form, in which synthetic polymers occur in molded plastics, and that biology does use continuous polymer fiber reinforcements but not mineral fiber reinforcements.

Collagen is of particular interest because the chains are wound into triple helices of about 640 nm length which are hydrogen bonded into fibrils. This discontinuous structure reduces the fiber strength when compared to silk or cellulose.

If we now compare the matrix phase of bone with that of the epoxy in a carbon-fiber composite, we notice important structural differences. Dense bone is about 40 vol% mineral, 20 vol% water, and 40 vol% collagen. The collagen is essentially discrete, highly oriented fibers in a gel matrix. This is a soft but strong structure. In contrast, epoxy resin is usually highly cross-linked and relatively brittle (Figure 1). The toughness of the composite essentially derives solely from the weakness of the interfaces. Current trends in composites are to use thermoplastic matrices with better toughness but the constraints imposed by the need to infiltrate the polymer amongst the fibers drastically limits the molecular weight of the resin.

Thus if we set the water-sensitivity of biopolymers aside, there are clear parallels in structure and performance between the various biological polymers and the main groups of synthetics, but they nonetheless are often used in different ways.

If we turn our attention to the reinforcing fillers the differences are very clear. The main biological reinforcements are calcium carbonate and hydroxyapatite. These relatively soft (Mohr hardness 3 and 5) compounds contrast with structural synthetic materials with higher hardness and internal bond strength such as silica, alumina, silicon carbide, and graphite. Harder materials are available to organisms, magnetite and silica do appear, but the improvement is clearly not sufficient to justify silica bones or magnetite shells. We can view this as an example of incompetence in the evolutionary system, as a reflection of metabolic costs dominating structural design or as a result of some improved control of precipitation and resorption for the crystalline calcium salts when compared to the oxides.

The form of the reinforcing phase shows substantial differences between natural and synthetic composites. Typical continuous fiber reinforcements have diameters of 10 microns. Many powders are used for particulate reinforcement of polymers but typical sizes are in the range of 0.1 microns to 20 microns. Bone is reinforced by platelets with a thickness of 4 nm, a width of 30-50 nm, and a length of 100-500 nm. This axial ratio,
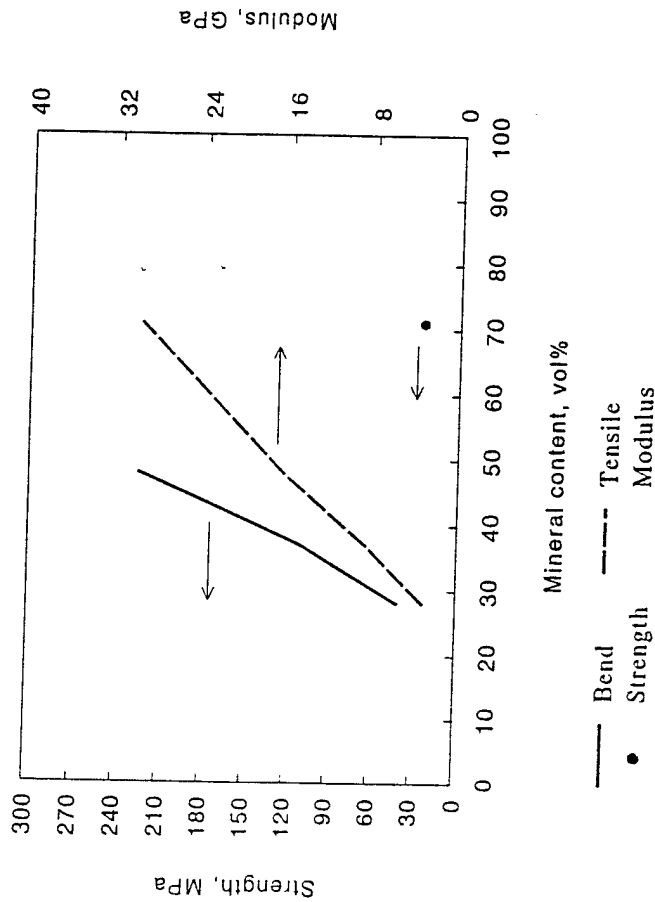
Figure 1. Properties of bone vs. mineral content.

of 20:1 or more, would be expected to give good load transfer from the matrix to the platelet if the interfacial bonding is strong.

Tooth and shell have such low organic contents that they are best thought of as ceramics. In enamel the hydroxyapatite crystals are about 40 nm wide by 150 nm long and bundled into larger rods, in shell the crystals have thicknesses of 0.5 μm by several microns wide. This scale is comparable with the sizes of the finest synthetic ceramics. The key differences lie in the presence of the organic layer surrounding the crystals and in the highly anisotropic shape of the crystals. Both of these factors may contribute to the higher toughness of natural ceramics when compared to synthetics. It is noteworthy

that small dentine crystals and large enamel crystals can be formed simultaneously and within a short distance of one another, controlled by local protein concentrations.

## 3.0 SYNTHETIC AND BIOLOGICAL COMPOSITES

Bone is a composite material where a tough collagen matrix is reinforced with hydroxy-apatite plates.[1] As such we would expect to be able compare the structure and mechanical properties of bone with those of equivalent reinforced polymer composites. Using theories for the modulus of composites with values for the moduli of the collagenous matrix and of hydroxyapatite, we can expect to predict the modulus of bone. This has been discussed by Currey in this book (page 115).

Table-I. Mechanical properties of bone and replacement materials for bone

| | Tensile Modulus, GPa | Bend Strength, MPa | $K_c$ MPa m$^{-1/2}$ | Toughness, $G_c$, Jm$^{-2}$ |
|---|---|---|---|---|
| Cortical bone | 7-30 | 50-150 | 2-12 | 600-5000 |
| Alumina | 365 | 6-55 | 3 | 40 |
| Ti Alloy | 106 | 900 | 80 | $10^4$ |
| PMMA | 3.5 | 70 | 1.5 | 400 |
| Polyethylene | 1 | 30 | | 8000 |
| Polyethylene-Hydroxyapatite, 40 vol%* | 5 | 22 | 3 | 1800 |
| Polyethylene-Hydroxyapatite, 50 vol% | 9 | 26 | 3 | 1000 |

*Bonfield et al.[13]

Strength is a less predictable property as it is more dependent on interfacial bonding and the detailed morphology of the composite. There have been efforts to reproduce the properties of bone for implant materials but, as shown in Table-I it is difficult to get a sufficiently high modulus without severely reducing the strength of analogous synthetic composites. This stems from the random packing which leads to fiber-fiber contacts and provides an easy fracture path.

of structures coupled with large variations in orientation and density across the bone. Some of the structure on the millimeter-centimeter scale, such as the Haversian system in human long bones may be due to reparability or damage limitation rather than performance.

Glass bead filling of synthetic polymers results in an increase in modulus and strength at the cost of a severe reduction in elongation to break. Reinforcement with glass fibers results in a significant increase in modulus and strength. Bigg[3] has recently reviewed fiber-filled thermoplastic composites. Strength and modulus can be predicted on the basis of the rule of mixtures. Both depend on aspect ratio, degree of orientation, and interfacial bonding as well as on the volume fractions and properties of the fibers and polymer. Aspect ratio is limited by the breakage of fibers that occurs during processing, especially at high volume fractions. As a result it is not practicable to use fiber volume fractions of more than about 0.3, beyond which strength starts to drop and the viscosity becomes too high for good molding. As shown in Figure 1, based on data from Currey,[4] bone shows a steady increase in strength to 50 vol% mineral. Beyond this, at about 70% there is effectively one set of data from the whale (ear) tympanic bulla, which shows high modulus but low strength. Since the function of this material is sound transmission rather than mechanical, it is difficult to know if it is representative of bone at high mineral fractions.

Bone is comparable in filler content and aspect ratio to the glass fiber filled polyethyleneterephthalate. It can be seen that the biggest difference in the two materials is the much larger extension to break of bone. This may well arise from the laminar structure of bone which provides weak planes. In this sense bone can exploit the hierarchy derived from a very fine, well bonded, filler combined with weak planes every few microns. In fiber composites we require the filler-matrix interface to be weak enough to deflect the fracture, yet strong enough to transfer load. These two functions seem to be separated in bone.

Sheet molding compound (SMC) is a composite of unsaturated polyester reinforced with long glass fibers and clay. It has a high modulus but at the cost of being formable only by bending the sheet before curing. This material is replacing metal for many car body panels. It can be seen that a bone-like material would be substantially better.

Table-II. Natural and synthetic composites

| | Elastic Modulus, GPa | Strength, MPa | Work of Fracture, kJ m$^{-2}$ | Fracture toughness, K$_{1c}$ MPa·m$^{-1/2}$ | Strain to break, % |
|---|---|---|---|---|---|
| Bone (bovine femur) | 20 | 220 | 1.7 | 5 | 10 |
| Insect cuticle (35 vol% chitin fibers) | 6-10 | 80 | | | |
| PEEK-Carbon fiber, 61 vol%, Longitudinal | 140 | 2200 | 1.6 | | 1 |
| PEEK-Carbon fiber, 61 vol%, Transverse | 8.3 | 73 | | | 1 |
| Polyethyleneterephthalate + 18 vol% glass fiber | 9 | 144 | | | 6.6 |
| Polyethyleneterephthalate + 35 vol% glass fiber | 20 | 165 | 3.2 | 9.5 | 1 |
| Sheet molding compound (35% glass fiber) | 16 | 158 | | | 1.7 |
| E Glass | 70 | 3,000 | | | |
| Hydroxyapatite | 130 | 100 | | | |
| Polyethyleneterephthalate | 3.3 | 60 | 7.3 | 4.9 | 275 |
| Collagen (tendon) | 2 | 100 | | | |

Data on synthetic composites from Reference 14.

Table-II compares bone with continuous fiber composites and with short fiber composites. Continuous fiber composites are very stiff and strong along the fiber axis but the properties are poor perpendicular to the fibers. In practice they also are extremely costly to process. Short fiber composites can be readily molded and are isotropic, but the properties are poorer. Bone seems to lie between these two groups. If we compare the structure of synthetic short fiber composites with bone, we see the following differences: bone mineral platelets are much finer than synthetic fibers, the packing densities are higher, interfacial bond strength is unknown but is probably similar to or higher than the matrix strength, the matrix is soft and tough rather than brittle, the filler is platy rather than fibrous and is highly aligned. The matrix is itself anisotropic and is oriented parallel to the filler. On the other hand the aspect ratio is in the range of 20-50 which is similar to composites.[2] The other challenging feature of bone is the hierarchy

Beyond these direct comparisons, one would like to be able to estimate the properties of a bone built from stronger materials than are available to the organism. Collagen is intrinsically weaker than other oriented polymers because the chains take the form of short, stiff rods. The comparison, in the table, of fracture of oriented collagen in tendon with yielding of isotropic polyethyleneterephthalate masks this difference. Similarly the tabulated fracture strength for hydroxyapatite is measured on bulk samples and so is much lower than it would be for the fine reinforcing plates. Hydroxyapatite is ionically bonded and glass or carbon are covalent and so should be intrinsically stronger when everything else is equal. One would expect much improved properties if a bone-like structure could be reproduced in a structure which was a dense mesh of oriented polyamide reinforced by very fine glass fibers with a high axial ratio.

## 4.0 SYNTHETIC AND BIOLOGICAL CERAMICS

We can compare natural and synthetic ceramics, as in Table-III. In doing this we regard nacre and enamel as ceramics, despite a small volume fraction of polymer in the structure. The natural materials are based on calcium salts with ionic bonding that is intrinsically much weaker than that of the oxide ceramics such as alumina. The interest here is in what strength and toughness can be achieved when viewed in some sort of relation to the intrinsic bond strength or to the modulus. Taken in this context the high work of fracture numbers must be regarded as very impressive. It is possible to ascribe this toughness to either the polymer fraction or to the high aspect ratio of the rods of hydroxyapatite in enamel and the plates of aragonite in nacre. In this context it is interesting to consider jade as a fibrous ceramic which is not polymer bonded but still retains much of the toughness.

Jackson et al. have discussed composite models for the mechanical properties of nacre.[5] Modulus is discussed in terms of shear-lag models and strength and toughness in terms of pull-out of the aragonite platelets in their polymeric envelope. He shows in Table-IV that the strength and toughness are much reduced if the shell is dried to the point of embrittling the polymer. We have similarly observed that a frozen clam shell is much more brittle than one at room temperature. Using the same model one can predict the strength of a similar polymer-bound ceramic structure formed with synthetic materials such as alumina and an engineering thermoplastic. Several hypothetical examples are given in Table-V.

The properties of these materials are impressive but applications as ceramics would be limited to below 300°C by the temperature sensitivity of the polymer. In tooth enamel there is no evidence that the small residual polymer fraction plays any mechanical role.

Table-III. Natural and synthetic ceramics

|  | Modulus, GPa | Strength, MPa | Gc, J m$^{-2}$ |
|---|---|---|---|
| Alumina | 350 | 100-1000 | 7 |
| Fused silica | 72 |  | 9 |
| Nacre | 64 | 130 | 600-1240 |
| Enamel | 45 | 76 | 13-200 |
| Jade (Jadeite) | 205 |  | 94-120 |

Table-IV. Properties of nacre

*Pinctada* nacre in fracture across the shell plane[15]

|  | Young's Modulus, GPa | Tensile Strength, MPa | Toughness, Gc, J m$^{-2}$ |
|---|---|---|---|
| Wet | 64 | 130 | 1240 |
| Dry | 73 | 167 | 464 |
| Dessicated |  |  | 264 |

Table-V. Estimated properties of nacre-like composites

| Polymer | Platelet | Volume Fraction, % | Young's Modulus, GPa | Tensile Strength, MPa |
|---|---|---|---|---|
| Polyphenylene sulfide | Alumina | 95 | 151 | 319 |
| Polyphenylene sulfide | Alumina | 80 | 83 | 269 |
| Polyphenylene sulfide | Silica | 95 | 43 | 319 |
| Epoxy | Alumina | 95 | 151 | 133 |

Calculated following the model for nacre in Jackson et al.[15]
Assuming a platelet thickness of 0.5 μm and aspect ratio of 8.

rounded by a lipid bilayer membrane. The magnetic particles in magnetotactic bacteria form similarly. In this case the membrane controls the influx of reagents. We know little enough about mechanisms of membrane transport and so cannot really guess how the conditions are established for precipitation within the vesicle. We would expect a combination of enzymes attached to the inside or outside membrane surface and transport proteins within the membrane.

The membrane may also act as a former to shape the growing particle, though sponge spicules often have a central polymer thread that is responsible for the initial shape formation.

Mineralization in synthetic lipid vesicles has been studied but the particles are usually grown by hydrogen ion, or other cation, transport into or out from the vesicle and there is little control over the deposition. Technically this process is unattractive because the low concentrations of vesicles and the low concentrations of ions in the vesicles severely limit the amount of material that can be formed. Scientifically we need more methods of control over ion transport and we need catalytic activity in the membrane before any interesting structures can be made.

The second group of mineralization processes are extracellular and so are more directly comparable to synthetic precipitation reactions. Tissues formed by this route include bone, tooth, and shell. In each case reagents must be delivered to a precipitation site and then the actual precipitation must be catalyzed locally.

Amongst the control mechanisms which may act in bone formation are nucleation sites, crystallization inhibitors, enzymes to break down inhibitors, enzymes to break down polyphosphates and create high concentrations of orthophosphate, impurity anions to control crystal size, and matrix orientation to control crystal orientation. Bone growth does also respond to local stresses but it is not known how the stress is sensed and transduced.

One clear ingredient in all these mineralizations is the presence of an extracellular matrix which structures the mineralization zone, prevents convection of reagents and particles, and allows localized concentrations.

Figure 2. Rat tooth enamel showing crossed rods of hydroxyapatite.

The polymer does seem to be responsible for breaking up the hydroxyapatite rods (Figure 2) into bundles of fine fibers which presumably limits the effective maximum flaw size to well below 1 μm. The properties of enamel should thus be reproducible in a synthetic ceramic, if we can devise a way of reproducing this structure.

## 5. MECHANISMS OF BIOMINERALIZATION

Biological composites apparently form by a wide variety of different methods such that only true principles governing their formation are rather general. All biological materials are made by aqueous processing at room temperature. The resultant structures are thus a product of direct chemical reaction rather than the result of thermally-induced changes.

If we focus on biomineralization, the processes clearly fall into two groups. Intracellular precipitation, such as sponge spicule formation, takes place within a vesicle sur-

Based on this analysis, we would like to be able to create composite and ceramic materials by precipitation within a polymeric matrix, and we would like to be able to demonstrate that such a matrix can specifically nucleate deposition, can have catalytic activity and can control orientation of the mineral. In addition we would like to be able to control particle size. With such a system we would hope to be able to form composites containing from 40-95 vol% of elongated sub-micron particles in a polymer. Such composites could be used as is, or sintered to a dense ceramic.

## 6.0 AVAILABLE SYNTHETIC ROUTES FOR IN-SITU CHEMISTRY

It is evident that mineralization of synthetic or biological polymers with calcium carbonate or hydroxyapatite, *in vitro* is quite feasible. Several groups are investigating precipitation of these compounds into proteins extracted from mollusks, into collagen and on variously treated synthetic surfaces. The approach can readily be extended to other sparingly soluble calcium carboxylates. We have prepared composites with potassium dihydrogenphosphate (KDP) in polyethyleneoxide by simple evaporation from an aqueous solution of polymer and salt. While such studies can teach us about the mechanism of biological mineralization, most of these materials are not intrinsically interesting. KDP is an exception because of its piezoelectric and non-linear optical properties.

Our own work has predominantly been concerned with the formation of oxide ceramic particles by hydrolysis of alkoxides from solution in polymers. We have grown particles of silica, titania, barium titanate, and zirconia. All these precipitates are initially amorphous but barium titanate, and presumably titania and zirconia, can be crystallized by treatment of the composite with boiling water.[6] This approach could obviously be extended to many other alkoxides. A number of metal chlorides such as iron (III) chloride and molybdenum (V) chloride, are highly soluble in organic solvents and can similarly be hydrolyzed *in situ* to oxides. In the case of iron, both magnetite and goethite can be formed.[7]

Reduction to metal *in situ* is also possible. Copper chloride has been reduced by sodium borohydride solutions to copper metal, as has iron(III) chloride. Sodium borohydride is not very penetrating and so tends to form surface films on polymers. Sodium

naphthalide is more organophilic and will cause precipitation throughout a film. In the case of iron, hydrogen will reduce to the metal but the high temperature needed also tends to degrade the polymer. Sulfides are also readily attainable, either by direct reaction with hydrogen sulfide gas or by treatment of a metal-containing polymer with bis-(trimethylsilyl)sulfide.

It is reasonable to assume that this approach can be extended to anything that can be prepared by solution chemistry at less than 150°C in aqueous or organic solution, or from the vapor phase. So far, these constraints exclude many high temperature materials of interest to ceramists, such as the carbides, nitrides and borides. It also excludes silicon and most other important semiconductors. We have formed silicon carbide by an analogy of the rice hull process, whereby silica was precipitated into cellulose film that was subsequently carbonized under an inert atmosphere. Heating this carbon-silica composite to 1400°C produced a crop of silicon carbide whiskers on the carbon. The fact that the whiskers grow up, like grass, suggests that the deposition is via silicon monoxide vapor rather than by carbonization of silica. It is to be hoped that the range of materials formable *in situ* will continue to expand.

## 7.0 CONTROL MECHANISMS FOR PRECIPITATION IN POLYMERS

The characteristics of *in situ* precipitation in polymers that we would like to duplicate synthetically include high volume fraction of particles, elongated particles of normally equiaxed crystals, oriented particles, catalysis of precipitation by the polymer leading to localization of the reaction, site-specific nucleation in or on the polymer, and finally control of particle size.

Our studies of particle development during alkoxide hydrolysis in polymers show that phase separation can occur during drying of the polymer film, or during subsequent hydrolysis. If phase separation occurs of liquid alkoxide from an essentially dry polymer, the scale of the particles which form is about 0.5 μm. If the alkoxide is more compatible with the polymer, phase separation does not take place until hydrolysis occurs and the particle size is much reduced, leading to an essentially transparent film. This compatibility can be tuned by modifying the polarity of the alkoxide group. Hyd-

rolysis in moist air also can give smaller particles than drying followed by hydrolysis, because the large fraction of residual solvent compatibilizes the matrix.

We have investigated the catalysis of particle formation by two ethylene-(aminated acrylate) copolymers. The high concentration of tertiary amine groups in the amorphous regions of this polymer lead to a high internal pH in the polymer and a strong tendency to swell in acid solvents. When this polymer is placed in a solution of acidified methanol, tetraethoxysilane, and water, the polymer swells strongly and entraps silica. This response may be an essentially passive reaction to the solvent. If the same solution is first allowed to react for some days, it becomes viscous but shows no precipitation. On adding the solid polymer, there is an uptake of silicic acid by the polymer and precipitation starts both in the polymer and in the surrounding solution. This must reflect both movement of the silicic acid into the basic regions within the polymer and exchange of hydrogen ions between the polymer and the solution.

This system is catalytic in the sense that the polymer drives the precipitation reaction, but it probably does so through the medium of hydroxyl ions rather than through the influence of the chain itself. In past studies of gout, it has been found that sodium urate precipitation preferentially occurs within the highly polar matrix of cartilage rather than in other tissues, despite the activity of sodium urate being constant throughout much of the body.[8] Here again, the matrix seems to catalyze precipitation by providing a favorable environment. We need to give some careful thought to the classification of matrix-particle interactions to define what we really mean in thermodynamic and kinetic terms when we talk about matrix control of precipitation.

The strength and toughness of biological composites depend on reinforcement by elongated and oriented particles. To achieve such reinforcement by biomimetic *in situ* precipitation we must be able to grow rods or plates in a polymer matrix. We have shown that plates can be formed by drawing a polymer film containing partly precipitated hydrated titania.[9] The aspect ratio can be controlled up to about 20. The plate thickness is less than 1 μm. This elongation process could be incorporated into injection molding or extrusion of polymers. A true mimic of biological mineralization would allow elongated particles to be grown during treatment of a preformed polymer component. We have shown that a two phase polymer containing rods of polymethyl-

methacrylate in polyvinylidene fluoride can be mineralized with titania. The titania particles form as "sausages" or rows, like peas in a pod, in the polymethylmethacrylate zones.[10]

Biomineralization controls particle size, shape and orientation to form strong composites containing high volume fraction of mineral. We have demonstrated similar types of control for growth of inorganic oxides in synthetic polymers, but not yet simultaneously in a single sample.

## 8.0 APPLICATIONS OF BIOMIMETIC COMPOSITES AND CERAMICS

In the short term, one goal of biomimetic materials can be seen as devising ways of reproducing biological microstructures in order to develop enhanced properties in synthetic ceramics and composites. A second aim is to produce materials that will function as surgical implants with better biological compatibility.[11] In the longer term we can hope to produce complex sensing and actuating structures by the use of *in situ* mineralization methods. This can involve the precipitation of magnetic, piezoelectric, or electro-optical materials into polymers and will take us into the field of intelligent materials.

In composites, potential applications of this approach include moldable filled polymers with very fine scale reinforcement, polymer films with hardened surfaces, moldings where the reinforcement direction is elongated along directions of highest stress and transparent composites.

In ceramics, there are clear benefits from lamellar structures with fine, toughening polymer layers.[12] The use of polymer limits the maximum operating temperature to about 300°C, but it is evident that we can also expect considerable toughening from elongated ceramic grains particles or fibers without polymer. These structures may be prepared by conventional multilayer ceramic processing or by methods derived from biomineralization.

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